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TECHNICAL MEMORANDUM 1282

THEORY OF FLAME PROPAGATION

By Y. B. Zeldovich

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THEORY OF FLAME PROPAGATION*

By Y. B. Zeldovich

The mechanism of flame propagation has been qualitatively formulated. In accordance with this formulation, the chemical reaction initiated in some layer brings about an increase in the temperature; because of the heat conduction, the temperature is raised in the neighboring layer where in turn the chemical reaction is initiated. In this manner the flame is propagated.

Michelson (reference 1) is credited with presenting the first reliable method for measuring the flame speed and for computing the temperature distribution in the preheated zone of burning gas. In various papers on the theory of the speed of combustion (Jouguet (reference 2), Nusselt (reference 3), Daniell (reference 4), and others), a solution is found only by making simplifying assumptions that do not correspond to the actual conditions. The comparatively unknown work of Taffanel (reference 5) is the most similar to present-day views.

In the work of Jost and von Muffling (references 6 and 7), Sachsse (reference 8), and particularly Lewis and von Elbe (reference 9), a method is formulated that is satisfied by theory, that is, the diffusion as well as the heat conductivity is considered, the concept of ignition temperature is not included, and the continuous dependence of the speed of reaction on the temperature and concentration is taken into account.

This method was first carried out in the work of D. A. Frank-Kamenetskii and the author (reference 10), in which an approximate method is given for the computation of the flame speed under definite rational assumptions concerning the chemical reaction and the constants of the explosive mixture.

The experimental work carried out at the Institute of Chemical Physics (reference 11) confirmed the validity of the theory.

In accordance with what has been previously stated, a more strict consideration of the problem, appears desirable, that is, an explanation

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of those general conditions that must be satisfied by an explosive mixture for the possible existence of the phenomenon of flame propagation; determination of a general method of computing the flame velocity for an arbitrary relation among rate of reaction, temperature, and concentration; and finally, determination and evaluation of the errors of the aforementioned approximate method (reference 10).

The present paper bears greater resemblance in its form to a mathematical than to a physicochemical investigation. The subject, however, is actually the physicochemical problem of the conditions under which the chemical reaction proceeds during combustion. The theory developed permits studying the rate of the reactions occurring at temperatures of 1500 to 3000°C for a time of the order of a millisecond to enable the measurement of the flame velocity. The mathematical apparatus provided is not complicated; the computation work is similarly not extensive particularly if it is compared with the difficulty of the direct experimental realization of the independent combustion of the gas and the direct measurement of the rapid homogeneous reaction under conditions approximating the flame conditions.

At the present time, investigations are being conducted and prepared for publication that concern concrete chemical systems that will extend our knowledge of the kinetics of the most important reactions to the region of high temperatures; and will provide a clear picture of the process of combustion of such propagated explosive mixtures as carbon monoxide - oxygen - nitrogen. Accordingly, a review of the present state of the theory that presents not only the final results but the entire basis of the theory, emphasizing the fundamental physical problems of the existence and properties of the solution in the general case, would seem desirable.

1. Equations of Heat Conductivity and Diffusion in a Flame

A two-dimensional flame is considered and the equation of heat conductivity giving the distribution of the temperatures and the equation of diffusion giving the distribution of the concentrations are set up; the total number of equations of diffusion is equal to the number of reacting substances and the products of the reaction. Only one equation of diffusion is written for the reacting substance of which there is a deficiency in the explosive mixture. In contrast to the classical problems of heat conductivity and diffusion, the liberation of heat and the consumption of the reacting substances that depends on the process of the chemical reaction are considered in the equations.

The following symbols are used;

- t time, (sec)
- x coordinate, x-axis perpendicular to plane of flame, (cm)
- ρ density of mixture, (g/cm³)
- u velocity of motion along x-axis, (cm/sec)
- T temperature, (deg)
- c specific heat at constant pressure, (cal/(deg)(g))
- k heat conductivity, (cal/(cm)(sec)(deg))
- a relative concentration of reacting substance in grams of substance per one gram of mixture (nondimensional)
- D coefficient of diffusion, (cm²/sec)
- Φ velocity of chemical reaction, (g/(sec)(cm³))
- h thermal effect of reaction, (cal/g)
- γ constant of thermal diffusion (nondimensional)

The equation of heat conductivity has the usual form

$$\rho c \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} k \frac{\partial T}{\partial x} - u \rho c \frac{\partial T}{\partial x} + h \Phi \quad (1)$$

The equation of diffusion may be written

$$\rho \frac{\partial a}{\partial t} = \frac{\partial}{\partial x} \left[D \rho \frac{\partial a}{\partial x} + \gamma \frac{D \rho a}{T} \cdot \frac{\partial T}{\partial x} \right] - u \rho \frac{\partial a}{\partial x} - \Phi \quad (2)$$

With change in temperature, the density of the gas is found to change greatly. The composition of the mixture is characterized by the magnitude a . The absolute value of the concentration, equal to $a \rho$ (g/cm³), changes because of gas expansion, diffusion, and reaction.

In equation (2) only processes that change the composition are considered and the expansion is excluded. The magnitude $D \rho (\partial a / \partial x)$ represents the mass flow of the substance carried along by the diffusion; in an isothermal diffusion, the flow is generally considered

to be proportional to the gradient of the absolute concentration ρa , that is, in the case $D \left[\frac{\partial(\rho a)}{\partial x} \right]$. In this case, however, the density ρ is practically constant and whether the mass flow is written as $D \left[\frac{\partial(\rho a)}{\partial x} \right]$ or $D\rho \left(\frac{\partial a}{\partial x} \right)$ is immaterial. In the nonisothermal case, the second form must be definitely chosen because, in the absence of thermodiffusion (separately considered by the second term $\gamma(D\rho a/T)(\partial T/\partial x)$) in a mixture of constant composition, there is no diffusive flow; that is, the flow is equal to 0 for $a = \text{constant}$, even if $\rho a \neq \text{constant}$ in this case.

Equation (2) may be obtained by a transformation of the equation for the absolute concentration

$$\frac{\partial}{\partial x} (\rho a) = \frac{\partial}{\partial x} \left(D\rho \frac{\partial a}{\partial x} + \gamma \frac{D\rho a}{T} \cdot \frac{\partial T}{\partial x} \right) - u \frac{\partial}{\partial x} (\rho a) - \rho a \frac{\partial u}{\partial x} - \Phi \quad (3)$$

by considering the equation of continuity

$$\frac{\partial \rho}{\partial t} = -u \frac{\partial \rho}{\partial x} - \rho \frac{\partial u}{\partial x} \quad (4)$$

The magnitude Φ represents the rate of consumption of the substance in the process of the chemical reaction; the rate of heat liberation in unit volume is equal to $h\Phi$. Φ is a function $\Phi(a, T)$ where $\Phi = 0$ for $a = 0$.

By considering the propagation of the flame, the velocity of motion of cold gas u_0 is sought for which the flame front is stationary and the entire distribution of T and a is independent of time. It is evident that u_0 is equal to the velocity with which the flame is propagated over the stationary cold gas but it is more convenient to consider the flow and the distributions of T and a as being independent of time. As the temperature rises in a gas flow, ρ drops and u increases in such a manner that the product ρu is constant at any point and equal to $\rho_0 u_0$. In equations (1) and (2), the left side $(\partial/\partial t)$ is equal to 0; the symbol $\partial/\partial x$ is replaced by d/dx . The following boundary conditions are imposed on $T(x)$ and $a(x)$:

$$\left. \begin{array}{lll} \text{for } x = -\infty & T = T_0 & a = a_0 \\ \text{for } x = +\infty & a = 0 & \end{array} \right\} \quad (5)$$

(because for $a \neq 0$ and $\Phi \neq 0$, the condition $a = \text{constant} \neq 0$ does not satisfy the equation).

It is likewise evident that for $x = \pm\infty$

$$\frac{dT}{dx} = \frac{da}{dx} = 0 \quad (5')$$

2. General Properties of Temperature Distribution

The general properties of $T(x)$ are found by integrating with respect to x from $-\infty$ to $+\infty$ in both equations.

$$\frac{d}{dx} k \frac{dT}{dx} - u\rho c \frac{dT}{dx} + h\Phi = 0 \quad (6)$$

$$\frac{d}{dx} \left(D\rho \frac{da}{dx} + \gamma D \frac{\rho a}{T} \frac{dT}{dx} \right) - u\rho \frac{da}{dx} - \Phi = 0 \quad (7)$$

By setting $T(+\infty) = T_2$,

$$u\rho c (T_2 - T_0) = h \int_{-\infty}^{+\infty} \Phi dx \quad (8)$$

$$u\rho a_0 = \int_{-\infty}^{+\infty} \Phi dx \quad (9)$$

$$T_2 = T_0 + \frac{ha_0}{c} \quad (10)$$

Equation (10) agrees with the result of the elementary computation of the combustion temperature by the energy balance. By considering equation (6), it is shown that T cannot pass through a maximum higher than T_2 because $\Phi \geq 0$; on the curve passing through the maximum, however, $dT/dx < 0$ and $(d/dx)(k dT/dx) > 0$, which according to equation (6) requires $\Phi < 0$.

In reference 1, incorrect assumptions are encountered, that is, for a rapid reaction of the gas heated to a certain temperature T_B higher than T_0 , a sudden increase in temperature occurs and

¹In the case of variable c , set $H = \int^{T_2} c dT$.

the following temperature is attained;

$$T_m = T_B + \frac{a_0 h}{c}$$

higher than $T_2 = T_0 + \frac{a_0 h}{c}$. Actually, if Φ is very large in a very narrow layer so that $\int \Phi dx$ is finite, then d^2T/dx^2 in this layer is very large, that is, in the limit as $\Phi \rightarrow \infty$, the magnitude dT/dx undergoes a discontinuity but T is continuous; an angle appears on the temperature-distribution curve (fig.1). It is also evident that the converse is really true; namely, that at all points at which Φ is finite or equal to 0, not only T but also dT/dx cannot undergo a discontinuity.

3. Relation Between Concentration and Temperature in Mixture of Gases of Approximately Same Molecular Weights

A mixture of gases of nearly the same molecular weights is next considered. In this case, it follows from the kinetic theory that practically no thermodiffusion occurs ($\gamma = 0$) and that the diffusion coefficient is related to heat conductivity by the expression²

$$k = cpD \quad (11)$$

The variable H is introduced (heat content or enthalpy), uniquely related to T as follows:

$$\left. \begin{aligned} H &= \int^T cdT \\ dH &= cdT \end{aligned} \right\} \quad (12)$$

²At room temperature, the heat conductivity of oxygen is 5.9×10^{-5} , nitrogen is 5.2×10^{-5} , carbon monoxide is 5.1×10^{-5} , and hydrogen is 40.7×10^{-5} . The product cpD for diffusion of oxygen - nitrogen is 5.8×10^{-5} , hydrogen - oxygen is 23×10^{-5} , hydrogen - nitrogen is 21×10^{-5} , and hydrogen - hydrogen is 38×10^{-5} .

The equations of heat conductivity and diffusion assume the similar forms

$$\frac{d}{dx} \frac{k}{c} \frac{dH}{dx} - u_p \frac{dH}{dx} + h\Phi = 0 \quad (13)$$

$$\frac{d}{dx} \frac{k}{c} \frac{da}{dx} - u_p \frac{da}{dx} - \Phi = 0 \quad (14)$$

from which

$$\frac{d}{dx} \frac{k}{c} \frac{d}{dx} (H + ah) - u_p \frac{d}{dx} (H + ah) = 0 \quad (15)$$

thus, by considering the boundary conditions (5') that will give

$$\frac{d}{dx} (H + ah) = 0 \text{ for } x = \pm \infty \quad (15')$$

the unique solution

$$H + ah = \text{constant} = H_0 + a_0 h \quad (16)$$

$$\left. \begin{array}{l} x = -\infty \\ H = H_0 \\ a = a_0 \\ x = +\infty \\ a = 0 \\ H = H_2 = H_0 + a_0 h \end{array} \right\} \quad (17)$$

The concentration is found to be uniquely related to the temperature (in the case of constant specific heat linearly: $cT + ah = \text{constant} = cT_0 + a_0h$) in such a manner that the total energy³ of a unit mass; the sum of the thermal and chemical energies is constant.

Lewis and von Elbe (reference 9) were the first to postulate the constancy of the total energy in all the intermediate layers in the flame by the assumption of a chain reaction that is brought about by the diffusion of active centers. From the previous discussion, it is evident that the constancy of the energy depends not on the mechanism of the reaction but on the ratio between the diffusion of the fuel and the heat conductivity of the mixture. As will be shown, the total energy is not constant for $D_{cp} \neq k$ in the region of combustion, but has a maximum or minimum value.

In considering the case $D_{cp} = k$, the velocity of the reaction $\Phi(a, T)$ may be expressed for known a_0, T_0 as a function of one variable magnitude a or T , or H because of the relation among the composition of the mixture, the temperature, and H .

The problem thus reduces to the consideration of the one equation

$$\frac{d}{dx} \frac{k}{c} \frac{dH}{dx} - u_p \frac{dH}{dx} + h \Phi(H) = 0 \quad (18)$$

in which $\Phi(H)$ is obtained from $\Phi(a, T)$ by the substitution of T and a from equations (12) and (16) so that for $H = H_2$, $\Phi = 0$ because for $H = H_2$, $a = 0$. Equation (18) may be solved under boundary conditions (17) and

$$\left. \begin{array}{l} x = -\infty \\ H = H_0 \\ x = +\infty \\ H = H_2 \end{array} \right\} \quad (18a)$$

³More accurately, the enthalpy (heat content) because the combustion occurs at constant pressure. See definition of C .

The product $u\rho$ is a constant magnitude that cannot, however, be considered as known; it is necessary to determine that value of $u\rho$ for which the equation has a solution satisfying the boundary conditions.

4. Condition of Existence and Uniqueness of Solution

The following nondimensional variables and parameters are introduced⁴:

$$\left. \begin{aligned} z &= \frac{H_2 - H}{H_2 - H_0} \\ y &= \frac{k}{c} \frac{\frac{dH}{dx}}{\sqrt{h (H_2 - H_0) \left(\Phi \frac{k}{c}\right)_m}} \\ \varphi(z) &= \frac{\Phi \frac{k}{c}}{\left(\Phi \frac{k}{c}\right)_m} \\ m &= \frac{u\rho}{\sqrt{\frac{h \left(\Phi \frac{k}{c}\right)_m}{H_2 - H_0}}} = \frac{u_0\rho}{\sqrt{\frac{1}{a_0} \left(\Phi \frac{k}{c}\right)_m}} \end{aligned} \right\} \quad (19)$$

where Φ_m , K_m , C_m are constants independent of a , H , and other magnitudes varying in the flame front. All finite results of the computations, particularly the magnitude of the velocity u , do not actually depend on the choice of Φ_m , K_m , and C_m . Because

$\varphi \sim \Phi_m^{\frac{1}{2}}$, it is found from equation (20) that $m \sim \Phi_m^{-\frac{1}{2}}$ and that

the velocity $u \sim m \Phi_m^{\frac{1}{2}}$ does not depend on Φ_m ; hence, the choice

⁴This convenient system was proposed by S.M. Fainberg in connection with work on the combustion of ozone.

of Φ_m , C_m , and K_m is arbitrary. For example, set

$$\left. \begin{aligned} K_m &= k (a = 0, T = T_2) \\ C_m &= C (a = 0, T = T_2) \\ \Phi_m &= \Phi(a_0, T_2) \end{aligned} \right\} \quad (19a)$$

It is noted that for $Dc\rho = k$,

$$z = \frac{a}{a_0}$$

By substituting and noting that

$$\frac{d}{dx} = \frac{dH}{dx} \frac{d}{dH}$$

the following equation is obtained in place of equation (18):

$$y \frac{dy}{dz} + my - \varphi(z) = 0 \quad (20)$$

with the boundary conditions

$$\left. \begin{aligned} z &= 0 \\ y &= 0 \\ z &= 1 \\ y &= 0 \end{aligned} \right\} \quad (21)$$

The conditions of the existence of a solution are considered. In the plane z, y the line $y_1 = \varphi(z)/m$ is drawn on which $dy/dz = 0$ (fig.2)⁵. For $y < y_1$, $dy/dz > 0$. From this condition it is evident

⁵ y_1 is not the integral curve of equation (20) but only one of the isoclinical equations.

that if $\varphi(z) > 0$ in the entire interval $0 \leq z \leq 1$, the curve satisfying the condition $y = 0, z = 0$ lies everywhere above the axis of abscissas and never (for any m) falls on the point $z = 1, y = 0$. This condition exists because near the point $z = 1, y = 0, dy/dz > 0$ and there are no curves from the region $z < 1, y > 0$ that pass through this point. Hence, in order that a solution exist, it is necessary that φ becomes 0 for $z \leq 1$.

The case considered first is where an even more strict condition is satisfied.

$$\varphi(z) = 0 \text{ for } z > \beta, \text{ where } \beta < 1 \quad (22)$$

(Note fig. 3.) Also, let $\varphi(z) > 0$ for $z < \beta$. The existence and uniqueness of the solution will be proven. The general theorems on the uniqueness of solution of a given differential equation are insufficient because the value of the coefficient m must be found.

Consider $y(z, m)$, a function of two variables, as satisfying constant m of equation (20) and the boundary condition $y(0, m) = 0$. The following equation is set up;

$$y_m = \frac{\partial y}{\partial m} \quad (23)$$

By dividing equation (20) by y and differentiating with respect to m

$$\left. \begin{aligned} \frac{dy_m}{dz} + \frac{\varphi(z)}{[y(z, m)]^2} y_m &= -1 \\ z &= 0 \\ y_m &= 0 \end{aligned} \right\} \quad (24)$$

In the region $0 \leq z \leq \beta, \varphi > 0$ and $y > 0$; it follows that $y_m < 0$.

Set

$$-y_m(\beta, m) = \epsilon \quad (25)$$

In the region $\beta \leq z < 1, dy_m/dz = -1$ so that

$$-y_m(1, m) = \epsilon + (1 - \beta) > 1 - \beta \quad (26)$$

Hence, dy/dm for $z = 1$ is always negative and an absolute value greater than a certain finite magnitude.

For $m = 0$, the initial equation can readily be solved as follows:

$$\left. \begin{aligned} y \frac{dy}{dz} &= \frac{1}{2} \frac{d}{dz} (y^2) = \varphi(z) \\ y &= \sqrt{2 \int_0^z \varphi(z) dz} \end{aligned} \right\} \quad (27)$$

$$y(z = 1, m = 0) = + \sqrt{2 \int_0^1 \varphi(z) dz} > 0 \quad {}^6(28)$$

As has been shown, as m increases, $y(z = 1, m)$ decreases monotonically and its derivative with respect to m is always finite. Thus, there is always one and only one m_0 for which

$$y(z = 1, m_0) = 0 \quad (29)$$

This value m_0 for which both conditions ($y = 0, z = 0$ and $y = 0, z = 1$) are satisfied will give, by formulas (19), the required flame velocity.

The practical method of finding m for a given $\varphi(z)$ and a given arbitrary value m_1 consists of finding the corresponding $y(z = 1, m_1)$ by numerical integration of equation (20) from the point $z = 0, y = 0$. If $y(z = 1, m_1) > 0$, another $m_2, m_2 > m_1$, is chosen and the numerical integration is again carried out; if $y(z = 1, m_1) < 0, m_2 < m_1$ is chosen. Several values of $y(z = 1)$ are found for various $m = m_1, m_2, m_3$ and are chosen so that some of

⁶If the other sign of the root is taken, the sign of m changes, that is, the propagation is considered in the reverse direction but all the physical conclusions remain valid.

the values found for $y(z=1)$ are positive and some negative. By laying off on a graph $y(z=1, m)$ as a function of m , the value of m_0 for which $y(z=1, m_0) = 0$ is found by interpolation.

As a result, the velocity of combustion is obtained by the formula

$$U_0 = \frac{m_0}{\rho_0} \sqrt{\frac{1}{a_0} \left(\Phi \frac{k}{c} \right)_m} \quad (30)$$

where m_0 represents a nondimensional number determined by the function Φ , that is, by the curve of $\Phi k/c$ as a function of H (or of the temperature). The dependence of the flame velocity on the absolute values of the reaction velocity and the heat conductivity is given by the root of formula (30). In considering the dependence on the composition of the mixture, it is necessary to take into account that a_0 is an important factor in the expressions for Φ and Φ_m because in passing from $\Phi(a, T)$ to $\Phi(H)$, a_0 entered formula (16) relating a and H .

By knowing m_0 and the corresponding integral curve $y(z, m_0)$, the law of distribution of H , T , and a in space as a function of x can also be found. For this determination, a single quadrature is sufficient that can always be carried out numerically

$$\begin{aligned} dx &= \frac{\frac{k}{c} dH}{y(z) \sqrt{h(H_2 - H_0) \left(\Phi \frac{k}{c} \right)_m}} = \frac{\frac{k}{c} (H_2 - H_0)}{y(z) \sqrt{h(H_2 - H_0) \left(\Phi \frac{k}{c} \right)_m}} \frac{dz}{y(z)} \\ &= -\sqrt{a_0 \frac{1}{\Phi_m} \frac{k_m}{c_m} \left(\frac{k}{k_m} \cdot \frac{c_m}{c} \right)} \frac{dz}{y(z)} \end{aligned} \quad (31)$$

where the subscript m denotes all the scalar magnitudes (see equations (19a)). The expression under the radical represents a constant magnitude having the dimension of a length and the expression in parentheses is a nondimensional ratio depending on z .

$$x = -\sqrt{a_0 \frac{1}{\Phi_m} \cdot \frac{k_m}{c_m}} \int^z \left(\frac{k}{k_m} \cdot \frac{c_m}{c} \right) \frac{dz}{y(z)} \quad (32)$$

By the given condition, $x = -\infty$ for $z = 1$ and for $x = +\infty$, $z = 0$. Near $z = 1$, $y(z) = m(1 - z)$ that gives, after substituting the value \underline{m} , the known Michelson solution

$$\left. \begin{aligned} x &= \frac{k_0}{c_0 \rho_0 u_0} \ln (T - T_0) + \text{constant} \\ T &= T_0 + \text{constant} \cdot \exp \left(\frac{k_0 x}{c_0 \rho_0 u_0} \right) \end{aligned} \right\} \quad (33)$$

Thus $T \rightarrow T_0$ only asymptotically as $x \rightarrow -\infty$. The behavior of the solution near $z = 0$, that is, where the reaction ends, depends on the form of $y(z)$ near $z = 0$, which in turn is determined by the expression of $\varphi(z)$ for small z .

If $\varphi(z)$ increases near $z = 0$, according to the law

$$\begin{aligned} \varphi(z) &= \text{constant } z^n \\ n &\geq 1 \end{aligned} \quad (34)$$

it is easy to show that

$$y(z) < \frac{\varphi}{m} \quad (35)$$

so that if the integral $\int_0 dz / \varphi(z)$ diverges, the integral $\int_0 dz / y(z)$ likewise diverges. In the absence of diffusion and heat conduction for an adiabatic reaction in a closed vessel, the magnitude z varies according to the equation

$$\frac{dz}{dt} = -A \varphi(z) \quad (36)$$

where $A = (1/a_0) (\Phi k/c)_m (c/k\rho)$ in the limit for small z approaches a constant value. Thus, if the integral $\int_0 dz / \varphi(z)$ diverges,

then, under adiabatic conditions, the chemical reaction comes to an end only asymptotically at $t \rightarrow \infty$. Correspondingly, in considering the problem of flame propagation, the end of the reaction $a = 0$, $T = T_2$, and $H = H_2$ is reached only in the limit at an infinite distance from the flame front.

The reverse case for small z is considered.

$$\left. \begin{aligned} y(z) &= \text{constant} \cdot z^{\frac{n-1}{2}} \\ \frac{n+1}{2} &< 1 \end{aligned} \right\} \quad (37)$$

In this case,

$$\left. \begin{aligned} \varphi(z) &= \text{constant} \cdot z^n \\ n &< 1 \end{aligned} \right\} \quad (38)$$

Thus, in the case where the integral $\int_0 dz/\varphi(z)$ is finite, the integral $\int_0 dz/y(z)$ is likewise finite and converges near $z = 0$.

Physically, the chemical reaction concerned goes to completion after a finite time under adiabatic conditions (in a closed vessel). In the presence of diffusion and heat conduction, the chemical reaction in the flame is likewise found to go to completion at a finite distance from the flame front (more specifically, at a finite distance from the place of most intense reaction). By computing $\int_0 dz/y(z)$ (for example, arbitrarily giving $x = 0$ for that value of z for which $\varphi(z) = \text{maximum}$), x_k is found for which

$$\left. \begin{aligned} x &= x_k \\ a &= 0 \\ H &= H_2 \\ T &= T_3 \\ \frac{dT}{dx} &= 0 \end{aligned} \right\} \quad (39)$$

The distribution of the concentrations and temperatures for $x < x_k$ is given by the integral (32). For any

$$\left. \begin{aligned} x &> x_k \\ a &\equiv 0 \\ H &\equiv H_2 \\ T &\equiv T_2 \\ z &\equiv 0 \end{aligned} \right\} \quad (40)$$

Thus, in the case of finite $\int_0 dz/\phi$, a singular point at $x = x_k$ appears in the distribution of $a(x)$, $T(x)$, and $H(x)$. At this singular point, two different solutions, relations (32) and (40), meet and the values of the magnitudes T , a , and H and their first derivatives with respect to x are the same on both sides⁷. The second or even higher derivative, however, may suffer a discontinuity, particularly if

$$\begin{aligned} \phi(Z) &= \text{constant } z^n \\ -1 &< n < 1 \end{aligned}$$

near $z = 0$,

$$T_2 - T = \text{constant } (H_2 - H) = \text{constant} \cdot a = \text{constant } (x_k - x)^{\frac{2}{1-n}} \quad (41)$$

where from the conditions⁸ imposed on the exponent, it follows that the degree of $(x_k - x)$ is positive and greater than 1 so that $T_2 - T = 0$ and $dT/dx = 0$ for $x \rightarrow x_k$.

⁷The first derivatives can have a discontinuity only for $\phi \rightarrow \infty$.

⁸The condition $n < 1$ follows from the requirement of the finiteness of $\int_0 dz/\phi$; otherwise, as has been shown, there is no singular point on the curve. The condition $1 < n$ follows from the requirement of the finiteness of $\int_0 \phi dz$. As will be shown, if this integral diverges, the magnitude m and the flame velocity are infinite; however, $n < 0$ already leads to infinite velocity of reaction for $a \rightarrow 0$, which is physically unreal.

The relations (32) and (40) thus give a complete solution satisfying equation (18) and boundary conditions (18a). The fact that the boundary condition $H = H_2$ is satisfied not only for $x = \infty$ but also for all $x > x_k$ does not contradict or prevent the solution from being considered correct. The part played by $\int_0 dz / \varphi(z)$

was pointed out to the author by V. I. Skobelkin but the author cannot agree with the opinion of Skobelkin that for the existence of a solution it is necessary that this integral diverge.

A solution has been shown to exist only in the case where for $z = 1$, $\varphi = 0$, that is, in the case where the reaction velocity is 0 in the initial mixture; for $T = T_0$, $a = a_0$. The solution has been found under the still more rigorous condition (22). This result is in no way an indication of the insufficient generality of the theory and the inapplicability of the theory to any case of flame propagation. On the contrary, this result entirely corresponds to those physical conditions that must exist in order that a strictly stationary process of flame propagation can occur. Not in every system in which the process of a chemical reaction is thermodynamically possible will flame propagation be observed, that is, the propagation in the space of the region of chemical reaction. For this flame propagation, it is necessary first of all that the heat given out during the reaction accelerate the process of the reaction in the neighboring layer. This condition, however, is still not sufficient; it is also necessary that in the initial state, that is, in the state in which the mixture is found at $x = -\infty$ at an infinite distance from the flame front at the initial temperature T_0 , the reaction velocity is strictly equal to 0. If this condition is not satisfied, a certain finite time may be found during which the mixture, which at the initial instant is in the initial state, reacts in the absence of external actions. This phenomenon can be illustrated by imagining an explosive mixture in an infinitely long pipe. If at the initial instant the mixture throughout is in the initial state except at the origin of coordinates where the flame is situated, the time required for the flame to reach a definite point in the pipe is equal to the distance of this point from the origin of coordinates divided by the flame velocity. An element of volume of the mixture with a finite reaction velocity at T_0 and at a sufficiently long distance from the origin reacts before the flame reaches it. As a result of the reaction as the flame is propagated, the properties of the mixture situated ahead of the flame front at infinity vary. Hence, for $\Phi(T_0, a_0) \neq 0$, the required regime of steady flame propagation is actually physically impossible and the absence of a solution of the equation in this case entirely agrees with the physical picture.

The peculiar mathematical difficulties arising in the consideration of reactions for which $\varphi(z=1)$ becomes 0, for example, proportional to $(1-z)$, is considered. In the case of heat propagation, there is no significance in investigating the flame velocity on the assumption that for T near T_0 , the reaction velocity is proportional to $(T - T_0)$ because it is experimentally possible to vary T_0 so that the flame propagation does not change. If for some $T_0 = T_{01}$, Φ is set equal to constant $(T - T_{01})$, then by this assumption, the case previously considered, $\varphi(z > \beta) = 0$ where $\beta < 1$, is obtained for $T_{02} < T_{01}$; for $T_{03} > T_{01}$, $\varphi(1) \neq 0$ is obtained, that is, the impossibility of a steady propagation. Thus, in the heat propagation the assumption $\Phi \sim (T - T_0)$, $\Phi \sim (1 - z)$ is a random one and unsuitable.

From general molecular-kinetic considerations it follows that at a low temperature near T_0 the velocity of the chemical reaction is finite and different from 0 but very small. In this sense, the existence of a steady flame propagation is an approximation because $\Phi(a_0, T_0) \neq 0$, but a very good approximation because $\Phi(a_0, T_0)$ is very small. By the law of Arrhenius, the velocity of the reaction at room temperature is of the order of e^{-30} or e^{-50} (for unity, the velocity at 3000°C was taken).

The curves of φ/m and y as functions of z are shown schematically in figure 4. For $z = 1$, $\varphi \neq 0$ but for $z > \beta_1$, $\varphi/m \ll y$. From a consideration of the equation, it follows that to obtain a solution it is necessary to set $\varphi(z) = 0$ for $z > \beta$; it is also easy to show that all numerical results (m , u , and the curve $T(x)$) depend very little on the choice of β (fig. 4, β_1 or the larger β_2) if $\varphi(z) \ll 1$ for $z > \beta_1$.

Thus, although the operation itself of cutting off $\varphi(z)$ at $z > \beta$ contains an arbitrary element in the choice of β , the cut-off is required and arbitrariness in the choice does not lead to arbitrariness in the results. In this sense, the theory may be considered satisfactory.

5. Isothermal Chain of Flame Propagation

The cut-off by means of multiplication by $(1 - z)$ in the heat propagation of the flame is, as has been shown, a random one. In considering chain and autocatalytic reactions, however, the assumption that the velocity of the chemical reaction is proportional to the concentration of the final product formed in the reaction is of

interest. For example, if the transformation of A and B (their concentrations are denoted by a and b) is assumed to proceed with the collisions of the molecules of A and B according to the equation



then, by assuming a constant temperature, the possibility of flame propagation is obtained if the substance B transformed during the reaction diffuses in the neighboring layers where the pure substance A is contained and results in a chemical reaction of the two substances, in which the velocity constant is denoted by C. An equation identical to equation (20) is obtained with

$$\left. \begin{aligned} \phi(a, b) &= C \cdot a \cdot b \\ b &= a_0 - a \\ \phi_m &= C a_0^2 \\ \varphi(z) &= z(1 - z) \end{aligned} \right\} \quad (42)$$

In connection with the problem of the propagation of a chemical reaction, this problem was considered in the unpublished works of B. N. Skalov and O. M. Todes at the Institute of Chemical Physics during 1937 and 1938. The results of this work are given in reference 12. Attention has also been called to the very interesting work of A. N. Kolmogorov, I. G. Petrovskii, and N. S. Piskunov (reference 13), which was published in 1937. In this work concerning the equivalent biological problem, all the results of this problem obtained later at the Institute of Chemical Physics are presented in an accurate and clear form.

It has been shown that equation (20) for $\varphi(z)$ given in equation (42) has a solution satisfying the boundary conditions for all

$$\begin{aligned} m &> m_1 = 2 \\ u &\geq 2 \sqrt{\frac{C D a_0}{\rho}} \end{aligned} \quad {}^9(43)$$

⁹Solutions are also possible for $m < 2$ but these solutions require the existence of the region $z > 1$, $a > a_0$, and $b < 0$ in which $\phi < 0$, thus indicating their complete physical unreality.

The physical meaning of these solutions has been clarified. For $\phi(z)$, given by formula (42), even in the absence of diffusion, the initial distribution a and b in space may be given satisfying the condition $a = a_0$ and $b = 0$ for $x \rightarrow -\infty$, which gives the propagation of the reaction in space. As quoted from reference 13: "The apparent displacement of the substance from the left toward the right will actually be brought about here by the increase of its density at each point, entirely independent of the course of the process at other points." The time of the reaction according to the equation

$$\frac{da}{dt} = Cab = \frac{C}{\rho} a (a_0 - a) \quad (42a)$$

depends logarithmically on the initial value $a_0 - a$ that approaches infinity for $a_0 - a \rightarrow 0$ and $a \rightarrow a_0$. Given the distribution

$$a = a_0 (1 - e^{nx}) \quad (\text{for } x < 0) \quad (44)$$

that satisfies the condition $a \rightarrow a_0, x \rightarrow -\infty$ a linear dependence of the reaction time on the coordinate is obtained, which leads to an apparent displacement with constant velocity. The smaller n is the greater is this velocity. By considering the nonstationary problem that for the particular case (42) has the form

$$\frac{\partial a}{\partial t} = D \frac{\partial^2 a}{\partial x^2} - \frac{C}{\rho} a (a_0 - a) \quad (45)$$

Kolmogorov, Petrovskii, and Piskunov showed that as the time $t \rightarrow \infty$, the portion of the curve $a(x, t)$ on which the initial part of the change of a from a_0 to 0 occurs is displaced in space with a velocity approaching the minimum value that satisfies the steady-state equation

$$u = 2 \sqrt{\frac{CDa_0}{\rho}} \quad (45a)$$

and the distribution $a(x, t)$ approaches the solution of the steady-state equation. The physical result is confirmed that in

any case of local inflammation the reaction will be displaced with a velocity according to equation (45a) and that larger velocities are physically unreal.¹⁰

According to Skalov, the limiting maximum value of the velocity in the nonsteady problem may be found by elementary methods by considering the transformed equation

$$\frac{\partial a}{\partial t} = D \frac{\partial^2 a}{\partial x^2} - \frac{C}{\rho} a_0 (a_0 - a) \quad (46)$$

that agrees with equation (45) for $a_0 - a \ll a_0$. Equation (46) is considered throughout for the initial conditions $t = 0$, $a = a_0$ except for a small region near $x = 0$, where $a \ll a_0$. By setting

$$a = a_0 - q e^{\frac{C}{\rho} a_0 t} \quad (47)$$

the following equation of diffusion without sources is obtained for q :

$$\left. \begin{aligned} \frac{\partial q}{\partial t} &= D \frac{\partial^2 q}{\partial x^2} \\ q &= A \cdot \frac{1}{\sqrt{t}} e^{\frac{x^2}{4Dt}} \end{aligned} \right\} \quad (48)$$

$$a = a_0 - A \frac{1}{\sqrt{t}} e^{\frac{C}{\rho} a_0 t - \frac{x^2}{4Dt}} \quad (49)$$

The relation between x and t is found at the point at which $a = a' < a_0$, that is, the law of displacement in space for the given concentration a'

$$\frac{C}{\rho} a_0 t - \frac{x^2}{4Dt} = \ln (a_0 - a') - \ln A + \frac{1}{2} \ln t \quad (50)$$

¹⁰The unreality of a greater u may also be established by the method of a cut by considering the following relations: $\Phi = 0$, $a_0 - a < \epsilon$, $\Phi = Ca (a_0 - a)$, and $a_0 - a > \epsilon$ and by finding in this case the only value of m and the corresponding value of u . For $\epsilon \rightarrow 0$, $u \rightarrow 2 \sqrt{(c/p) Da_0}$.

In the limit as $t \rightarrow \infty$,

$$\left. \begin{aligned} x^2 &= \frac{4DCa_0 t^2}{\rho} \\ x &= t \cdot 2\sqrt{\frac{DCa_0}{\rho}} \\ u &\rightarrow 2\sqrt{\frac{C}{\rho} Da_0} \end{aligned} \right\} \quad (51)$$

which was required to be shown. The substitution of $(C/\rho) a(a_0 - a)$ by $(C/\rho) a_0(a_0 - a)$ is an overevaluation and can give only an increased but not a decreased velocity.

6. Approximate Formulas for Reactions Strongly Dependent on Temperature

Considering the theory of the thermal propagation of a flame, approximate expressions of the flame velocity are considered for the case where the velocity of the reaction increases rapidly with increasing temperature so that the function ϕ of equation (18) (in which a and T are already expressed in terms of H) has a sharp maximum for H near H_2 .

In equation (20), $\varphi(z)$ is shown to have a sharp maximum for $z \ll 1$. This case is of most interest for typical chemical reactions of combustion.

According to assumption (22) that $\varphi(z)$ is different from 0 only for $z < \beta$, a strict evaluation can be given of the upper and lower limits of the magnitude m in such form that for $\beta \rightarrow 0$, they approach the same value that is the limiting expression for m for small β .

The entire range of integration of z from 0 to 1 is divided into two parts: from 0 to β and from β to 1. In the second part

$$\left. \begin{aligned} \varphi &= 0 \\ \frac{dy}{dz} &= -m \\ y &= y(\beta) - m(z - \beta) \\ y(1) &= 0 = y(\beta) - m(1 - \beta) \end{aligned} \right\} \quad (52)$$

hence, it follows that

$$m = \frac{y(\beta)}{1 - \beta} \quad (53)$$

so that finding m reduces to determining $y(\beta)$, where an exaggerated value of $y(\beta)$ will give an exaggerated value of m . In the first range, the exaggerated value y_{\max} is obtained, rejecting the negative term my :

$$y \frac{dy}{dz} = \varphi - my < y_{\max} \frac{dy_{\max}}{dz} = \varphi \quad (54)$$

$$\left. \begin{aligned} y_{\max} &= \sqrt{2 \int_0^z \varphi dv} \\ y_{\max}(\beta) &= \sqrt{2 \int_0^\beta \varphi dv} = \sqrt{2I} \end{aligned} \right\} \quad (55)$$

where v is an auxiliary variable of integration and I denotes the integral $\int_0^\beta \varphi dv$. The limits of integration may also be extended to unity without markedly changing the integral because the case of the function φ is considered as having a sharp maximum at small $z < \beta$.

Thus, by taking

$$I = \int_0^1 \varphi dv \quad (56)$$

the upper limit of m is obtained

$$m < m_{\max} = \frac{1}{1 - \beta} \sqrt{2I} \rightarrow (1 + \beta + \dots) \sqrt{2I} \text{ for } \beta \ll 1 \quad (57)$$

In order to find the lower limit y_{\min} of y , the equation is written in the form solved for dy/dz and the dominating value $y_{\max}(z)$ from equation (55) is substituted on the right side for y .

$$\frac{dy}{dz} = \frac{\varphi}{y} - m > \frac{\varphi}{y_{\max}} - m = \frac{dy_{\min}}{dz}$$

$$y > y_{\min} = \int_0^z \frac{\varphi(v) dv}{y_{\max}} - mz = \int_0^z \frac{\varphi(v) dv}{\int_0^v \sqrt{2 \int_0^v \varphi(\omega) d\omega}} - mz = \sqrt{2 \int_0^z \varphi d\varphi} - mz \quad (58)$$

$$y(\beta) > y_{\min}(\beta) = \sqrt{2 \int_0^\beta \varphi dv} - m\beta = \sqrt{2I} - m\beta$$

$$m > m_{\min} = \sqrt{2I}$$

Thus, for small β , the upper and lower limits coincide and give the limiting expression

$$m = \sqrt{2I} = \sqrt{2 \int_0^1 \varphi dv} \quad (59)$$

Chemical kinetics generally lead to the expression

$$\Phi(a, T) = \text{constant} \cdot a^n e^{-A/RT} \quad (60)$$

which after transformation gives

$$\left. \begin{aligned} \varphi(z) &= Cz^n e^{-\frac{x}{1-\lambda z}} \\ \chi &= \frac{A}{RT_2} \gg 1 \\ \lambda &= 1 - \frac{T_0}{T_2} < 1 \end{aligned} \right\} \quad (61)$$

This expression may be approximately represented by making use of the assumption of Frank-Kamenetskii (reference 17) in the form

$$\varphi(z) = Ce^{-x} z^n e^{-x\lambda z} \quad (62)$$

which in agreement with equation (59) (considering the fact that $e^{-x\lambda} \ll 1$), gives

$$m = \sqrt{\frac{2Ce^{-x}}{(x\gamma)^{n-1}}} n! \quad (63)$$

Expressions (59) and (63) represent those approximate solutions that are given in references 10 and 15 where the physicochemical consequences of these results are given in detail. The less accurate but clearer derivation of these formulas directly from equations (6) or (18) in the coordinates x, T or x, H will not be repeated; as has been shown, a strict mathematical analysis confirms the correctness of this result. Expressions (60) and (62) do not become 0 for $T = T_0$ and $z = 1$. The numerical computation shows, however, that they are then very small (as exponents of large negative numbers). The principal difficulties connected with this and the method of overcoming them were previously explained. Evidently in cutting off $\varphi(z)$ in the region where $\varphi(z) \ll 1$, the part played by the magnitude β ($\varphi = 0$ for $z > \beta$) will be played by the magnitude μ/λ , where μ is of the order of several units.

In this manner, expression (63) and corresponding formulas of the previous work are correct in the limit when $x\lambda \gg 1$ (which corresponds to the case $\beta \ll 1$), that is, for

$$\frac{A(T_2 - T_0)}{RT_2^2} \gg 1 \quad (64)$$

as has been shown in references 10 and 15.

By the method of successive approximations, a correction of the order $1/\lambda$, $1/\lambda^2$ and their powers can also be obtained in expression (63) (see reference 16 for an example by P. G. Smirnov). In view of our present knowledge of the velocity of a chemical reaction and a number of idealized assumptions (for example, the absence of heat losses), however, such exactness is of no practical interest.

7. Case of Mixture of Gases of Different Molecular Weights

Those cases where the identical relation (16) between the concentrations and the temperature does not hold will be briefly considered.

Such a relation does not hold if:

a) $D_{cp} \neq k$ and $\gamma \neq 0$, which holds true in a mixture of gases differing considerably in their molecular weights.

b) Several (parallel or successive) chemical reactions take place in the flame and the relations between their equations and the velocity are such that the concentrations of the different chemical substances are not connected by algebraic relations.

In the first case, equations (6) and (7) must be considered. A nondimensional transformation analogous to equation (19) is again introduced. For exactness, $\Phi_m = \Phi(a_0, T_2)$ is taken for the unit of reaction velocity; $K_m = k(0, T_2)$ and $C_m = c(0, T_2)$ the values of the combustion products, are taken for the units of heat conductivity and heat capacity.

The nondimensional relative concentration α and the other nondimensional magnitudes already employed are also introduced.

$$\left. \begin{aligned}
 \alpha &= \frac{a}{a_0} \\
 z &= \frac{H_2 - H}{H_2 - H_0} \\
 \varphi(\alpha, z) &= \frac{k(a, T) \Phi(a, T) C_m}{C(a, T) K_m \Phi_m} \\
 y &= -\frac{c}{k} \frac{dz}{dx} \sqrt{\frac{C_m (H_2 - H_0)}{K_m \Phi_m}} \\
 m &= \rho u \sqrt{\frac{C_m (H_2 - H_0)}{k K_m \Phi_m}}
 \end{aligned} \right\} \quad (65)$$

$$H_2 - H_0 = h a_0$$

Expressed in these variables, the heat conductivity and diffusion are transformed into

$$y \frac{dy}{dz} + my - \varphi(\alpha, z) = 0 \quad (66)$$

$$y \frac{d}{dz} \mathfrak{J} y \frac{d\alpha}{dz} - y \frac{d}{dz} \theta \alpha y + my \frac{d\alpha}{dz} - \varphi(\alpha, z) = 0 \quad (67)$$

where

$$\mathfrak{J} = \mathfrak{J}(\alpha, z) = \frac{Dc\rho}{k}$$

$$\theta = \theta(\alpha, z) = \frac{\gamma D \rho (H_2 - H_0)}{kT}$$

The boundary conditions are $z = 0$, $y = 0$, $\alpha = 0$, $z = 1$, $y = 0$, and $\alpha = 1$. The nondimensional magnitudes \mathfrak{J} and θ characterize the ratio of the diffusion to the temperature conductivity and the thermodiffusion, respectively. In general, both magnitudes depend on the composition and the temperature, that is, they depend on the nondimensional variables α and z but they have neither singu-

larities nor zeros in the entire range of variation of α and z . At all times, $\vartheta > 0$; $\vartheta > 1$ for a mixture containing a small amount of a light gas (for example, $H_2 + O_2$ or $H_2 + Br_2$ in an insufficient quantity of hydrogen). As a rule, in mixtures in which $\vartheta > 1$, $\gamma < 0$, and $\theta < 0$ (in a thermodiffusion equilibrium, a light gas generally concentrates in the hot part of the vessel).

For $\vartheta = 1$ and $\theta = 0$, the system has the obvious solution $\alpha = z$, which was previously used. In the general case of arbitrary ϑ , θ , and $^{11}\varphi$, a method may be proposed analogous to that previously described that consists of the numerical integration of the equations for different m at the initial stream conditions for $z = 0$ and the choice of interpolation of such a value of m for which the solution satisfies the conditions for $z = 1$.

The difficulty is that according to the general theory for the integration of an equation of the second order for α , it is necessary for $z = 0$ to give, in addition to $\alpha = 0$, the derivative $d\alpha/dz$. An explanation is also necessary as to whether for one m both conditions $\alpha = 1$ and $y = 0$ will simultaneously be satisfied.

By dividing equations (66) and (67) by y and integrating, the following equation is obtained for the solutions satisfying the condition $\alpha = 0$, $y = 0$ for $z = 0$:

$$y(1) + m = \int_0^1 \frac{1}{y} dz = \left(\vartheta y \frac{d\alpha}{dz} \Big|_{z=1} - \vartheta y \frac{d\alpha}{dz} \Big|_{z=0} \right) - \theta \alpha(1) y(1) + m \alpha(1) \quad (68)$$

Hence, that value of m for which $y(1) = 0$ also satisfies $\alpha(1) = 1$ if $y d\alpha/dz = 0$ for $z = 0$ and for $z = 1$.¹²

¹¹On φ are imposed the conditions $\varphi = 0$ for $\alpha = 0$, $\varphi = 0$ in the neighborhood of $\alpha = 1$, $z = 1$, that is, $\Phi = 0$ for T , a near T_0 , a_0 in the initial mixture as is required for the existence of the propagation regime (see preceding discussion).

¹²The satisfying of $y = 0$ for $z = 0$ and $z = 1$ is not sufficient for this because $-d\alpha/dz$ may approach infinity.

Near $z = 1$, $\alpha = 1$, and $y = 0$ in the region in which $\varphi = 0$, the equations reduce to the system

$$\left. \begin{aligned} \frac{dy}{dz} &= -m \\ y &= m(1-z) \\ \frac{d}{dz} \vartheta(1-z) \frac{d\alpha}{dz} - \frac{d}{dz} \theta \alpha(1-z) + \frac{d\alpha}{dz} &= 0 \end{aligned} \right\} \quad (69)$$

By retaining the principal terms (for small $1-z$)¹³

$$\begin{aligned} \frac{d^2\alpha}{dz^2} &= \left(1 - \frac{1}{\vartheta}\right) \frac{1}{1-z} \frac{d\alpha}{dz} - \frac{\theta}{1-z} \\ \frac{d\alpha}{dz} &= \frac{\theta}{1 - \frac{1}{\vartheta}} + \text{constant} (1-z)^{\frac{1}{\vartheta} - 1} \end{aligned} \quad (70)$$

Thus, by whatever law the curve $\alpha(z)$ approaches the point $z = 1$, for that value of m at which point $y = 0$,

$$y \frac{d\alpha}{dz} = m(1-z) \frac{d\alpha}{dz} \equiv 0$$

for $z = 1$ also in the case ($\vartheta < 1$) where $d\alpha/dz \rightarrow \infty$ for $z = 1$. For obtaining m , it is therefore sufficient to give

$$\left. \begin{aligned} z &= 0 \\ y &= 0 \\ \alpha &= 0 \\ y \frac{d\alpha}{dz} &= 0 \end{aligned} \right\} \quad (71)$$

¹³The values of ϑ and θ in equation (70) are taken for $z = 1$, $\alpha = 1$.

and find the value of m for which the solution satisfies $y = 0$ for $z = 1$; the conditions $\alpha = 1$ and $z = 1$ will be automatically satisfied.

By assuming φ for small α in the form $\varphi = \alpha^n \psi(z)$ where $\psi(0) \neq 0$, the following relations are obtained for small $z \ll 1$:

$$\begin{aligned}\alpha &= z \text{ for } n > 1 \\ \alpha &= \frac{z}{\vartheta} \text{ for } n < 1 \\ \alpha &= z \left\{ \vartheta + (1 - \vartheta) \left[\sqrt{\frac{m^2}{\psi(0)} + \left(\frac{m^2}{2\psi(0)} \right)^2} - \frac{m^2}{2\psi(0)} \right] \right\}^{-1} \text{ for } n = 1\end{aligned} \quad (72)$$

As a rule, in the combustion of gases, the function φ has the form:

$$\varphi(\alpha, z) = \text{const } \alpha^n e^{-A/(1-\lambda)} \cong \text{const } \alpha^n e^{-A\lambda z} \quad (73)$$

where $A = E/RT_\Gamma > 1$.

The coefficient A usually lies between 7 and 20 and $\lambda = (T_2 - T_0)/T_2$, $1 - \lambda = T_0/T_2$ generally lies between 1/4 and 1/10. For $z = 0$ and $\varphi = 0$, the following relation is obtained for very small z :

$$z < \frac{1}{A\lambda} \ll 1$$

φ increases with increasing z because of increasing α but with further increase in z , φ rapidly (exponentially) drops. The region of maximum φ near $z = n/A\lambda \ll 1$ is of principal effect for the integral $\int \varphi dz$.

From estimates (57) and (58) previously made, it follows that

$$m \cong y_{\max} \cong \sqrt{\frac{1}{2 \int_0^1 \varphi dz}}$$

In the principal region near maximum φ and maximum y

$$my \cong 2 \int \varphi dz \cong \frac{n}{A\lambda} \varphi_{\max} \ll \varphi_{\max} \cong y \frac{dy}{dz} \quad (74)$$

whence, in the region of chemical reaction, the principal terms of equation (67) are

$$\varphi(\alpha, z) \cong y \frac{d}{dz} y \frac{d\alpha}{dz}$$

(the terms rejected are less than the remaining terms in the ratio $n/A\lambda$) therefore, it follows that in this region

$$\left. \begin{aligned} y \frac{d}{dz} y \frac{d\alpha}{dz} &\cong y \frac{dx}{dz} \\ \frac{d\alpha}{dz} &\cong \frac{1}{y} \\ \alpha &\cong \frac{z}{y} \end{aligned} \right\} \quad (75)$$

independent of the value of m determining the ratio of α and z in the limit for very small z .

The result given, valid in the limit for very large heat of activation (greater than A), was pointed out by L. L. Landay.

For this limiting case, the following simple formula is obtained for the flame velocity:

$$m = \sqrt{2 \int_0^1 \varphi dz} \quad (76)$$

where

$$\varphi = \varphi(a, z) = \varphi\left(\alpha = \frac{z}{y}, z\right)$$

Thus, in the case of a reaction with large heat of activation, the velocity of which is $\Phi \sim a^n$, the flame velocity computed by the elementary theory (59) for $D_{cp} \neq k$ must be multiplied by $(D_{cp}/k)^{-n/2}$ in order to obtain the true value; for Φ , an arbitrary function of a must be substituted in Φ

$$a = a_0 \frac{k}{D_{cp}} \frac{H_2 - H}{H_2 - H_0} \text{ for } \frac{H_2 - H}{H_2 - H_0} \ll 1 \quad (77)$$

From the form of the distribution of a and T in space, conclusions were drawn by the author concerning the instability of the plane wave front relative to its curving for $D_{cp} > k$ (reference 15). The physical properties of such mixtures were confirmed in the experimental work of Drozdov and Zeldovich (reference 17).

8. Equation of An Exothermal Chain Reaction

The case of several chemical reactions is very common. To describe the combustion of a mixture with chain kinetics, considering at least two concentrations is necessary, namely those of the initial substance a and the active centers and of the active intermediate product b . In a number of papers by N. N. Semenov, his followers, and the Institute of Chemical Physics a large number of active centers were found to be formed in oxidation reactions, thus providing additional basis for expecting such to be the case in flames.

In certain cases, because of definite relations between the concentrations, the problem can be reduced to the case of a single reaction. Thus, in the case of ozone in the presence of a rapid reversible reaction, as considered by Lewis and von Elbe (reference 9), a balanced thermodynamic relation is established between the concentrations of the active centers and the initial substance. In a rapid transformation of the initial substance into active centers with the liberation of a large amount of heat, the velocity of the flame propagation is determined by the single first reaction; the succeeding slow transformation of the centers into the final substances does not affect the flame velocity. From the mathematical point of view, these cases are trivial. In the most frequently encountered nontrivial case, however, the transformation of a into b generally occurs with a small liberation of heat with a large heat of activation and autocatalysis of b ; the transformation of b into the final products is accompanied by the liberation of a large amount of heat and depends little on the temperature. The system of equations for an idealized typical chain reaction is used as an example.

Let the reaction be such that in a closed and heat-insulated vessel, the equations of kinetics and the changes in temperature have the form

$$\left. \begin{aligned} \rho \frac{da}{dt} &= -B_1 a b e^{E/RT} \\ \rho \frac{db}{dt} &= B_1 a b e^{-E/RT} - B_2 b^2 \\ c\rho \frac{dT}{dt} &= hB_2 b^2 \end{aligned} \right\} \quad (78)$$

The equations of propagation for $Dc\rho = k$, $\gamma = 0$, and for the additional simplifying assumptions, $k = \text{constant}$ and $c = \text{constant}$, in nondimensional variables may be written as

$$y \frac{dy}{dz} + my - \beta^2 = 0 \quad (79)$$

$$y \frac{d}{dz} y \frac{d\alpha}{dz} + my \frac{d\alpha}{dz} - B\beta\alpha e^{-A_1 z} = 0 \quad (80)$$

$$y \frac{d}{dz} y \frac{d\beta}{dz} + my \frac{d\beta}{dz} - \beta^2 + B\beta\alpha e^{-A_1 z} = 0 \quad (81)$$

where

$$B = \frac{B_1}{B_2} e^{-E/RT}$$

$$E_1 = E_1 \frac{T_2 - T_0}{RT_2^2}$$

$$\alpha = \frac{a}{a_0}$$

$$\beta = \frac{b}{a_0}$$

where a_0 is the initial concentration of the substance and the remaining nondimensional variables are the same as previously defined with the following conditions: $z = 0$, $\alpha = 0$, $\beta = 0$, $y = 0$, $y d\beta/dz = 0$,

$$z = 1$$

$$\alpha = 1$$

$$\beta = 0$$

$$y = 0$$

$$y \frac{d\alpha}{dz} = 0$$

$$y \frac{d\beta}{dz} = 0$$

The following equation is easily obtained

$$y \frac{d}{dz} y \left(\frac{d\alpha}{dz} + \frac{d\beta}{dz} - 1 \right) + my \left(\frac{d\alpha}{dz} + \frac{d\beta}{dz} - 1 \right) = 0 \quad (82)$$

where

$$a = z - \beta$$

In this manner the two following equations are derived;

$$y \frac{dy}{dz} + my - \beta^2 = 0$$

$$y \frac{d}{dz} y \frac{d\beta}{dz} + my \frac{d\beta}{dz} - \beta^2 + B\beta (z - \beta) e^{-A_1 z} = 0 \quad (83)$$

For $1 < z \gg 1/A_1$, set $e^{-A_1 z} \equiv 0$.

At the present time, the method of finding the value of m in such a system is not clear. In the most practical case of the combustion of hydrogen with oxygen (in this case, all the constants entering the equation may be assumed as known), the problem is made still more complicated by the fact that $D_{cp} \neq k$ and that δ_a and δ_b are introduced in equations (83) so that it is necessary to con-

sider a system of three equations. The principal difficulty, however, is in the behavior of the solutions in the neighborhood of singular points and the conditions of the simultaneous satisfying of the boundary conditions by all the variables. The numerical integration of a system of ordinary differential equations for different values of one parameter does not offer special difficulties.

SUMMARY

1. Equations are set up for heat conductivity and diffusion considering the chemical reaction in the flame propagated in an explosive mixture.
2. General properties of the temperature distribution in the flame are presented.
3. Conditions are described that must be satisfied by the chemical reaction so that a regime of flame propagation with constant velocity would be possible.
4. For a definite relation between diffusion and heat conduction, a method is given for determining the flame velocity from the equation by numerical integration; the uniqueness of the method is also shown.
5. An estimate in quadratures is given of the upper and lower limits of the flame velocity; with increasing temperature dependence of the velocity of reaction, both limits approach each other, tending toward a value that was given in previous papers on the basis of physical considerations.
6. A method of solution and the limiting value of velocity for an arbitrary relation between diffusion and heat conduction are given.
7. Equations are set up for the flame propagation in a chain reaction.

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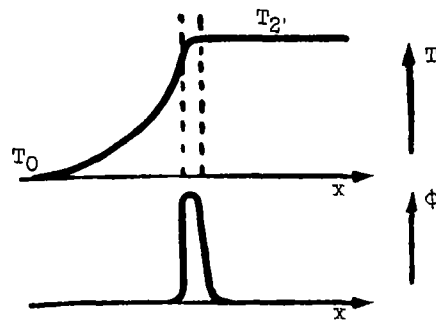


Figure 1.

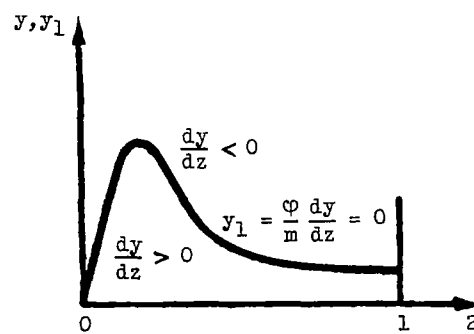


Figure 2.

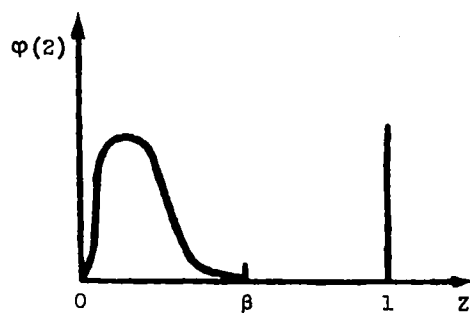


Figure 3.

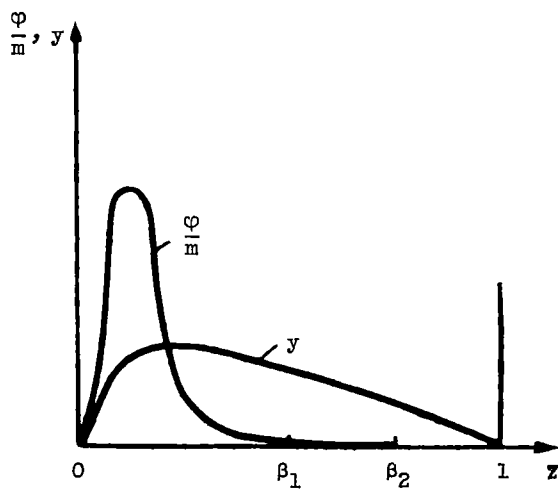


Figure 4.

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